

Interactions and magnetism in graphene boundary states

B. Wunsch^{1,2}, T. Stauber^{2,3}, F. Sols¹ and F. Guinea²

¹ *Departamento de Física de Materiales, Universidad Complutense de Madrid, E-28040 Madrid, Spain.*

² *Instituto de Ciencia de Materiales de Madrid, CSIC, E-28049 Madrid, Spain. and*

³ *Departamento de Física, Universidade do Minho, P-4710-057, Braga, Portugal*

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We analyze interaction effects on boundary states of single layer graphene. Near a half filled band, both short and long-ranged interactions lead to a fully spin polarized configuration. In addition, the band of boundary states acquires a finite dispersion as function of the momentum parallel to the edge, induced by the interactions. Away from half filling the wavefunction develops charge correlations similar to those in a Wigner crystal, and the spin strongly alternates with the occupation of the boundary states. For certain fillings the ground state has a finite linear momentum, leading to the formation of persistent currents.

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Introduction. The relativistic low energy properties of graphene give rise to many anomalies with respect to semiconductor physics and are thus very interesting from a fundamental point of view [1, 2]. Furthermore, carbon-based nanoelectronics have attracted much interest as they might complement silicon-based devices [3]. An important question concerns the magnetic properties of graphene. While ideal graphene sheets are far away from the ferromagnetic phase transition [4], the occurrence of midgap states, that lead to a peak in the density at the Dirac points, can lead to magnetism.

The most studied example of midgap states are boundary states [5, 6, 7]. Depending on the kind of edge there is a mismatch between the number of *A* and *B* sites and Lieb theorem (strictly applicable only to Hubbard interaction) guarantees a magnetic ground state at half filling with a spin given by $S = (N_A - N_B)/2$ [8]. A prominent example are zigzag-edges where the outermost atom corresponds always to the same site. However, boundary states are present not only for zigzag edges but for any boundary except for pure armchair edges [6, 9]. The originally flat energy band of boundary states is strongly affected by electron-electron interactions and first principle calculations predict magnetic boundaries [10, 11, 12, 13].

Previous approaches mostly consider the short-ranged Hubbard interaction. However, in graphene the screening close to half filling is known to be poor [14] and a comparison with results considering the more realistic case of long-ranged Coulomb interactions is therefore desirable. For extended systems and finite doping, this is typically done within the random phase approximation [15, 16]. The effect of interaction on the flat band of midgap states however is better described by non-perturbative treatments [17].

In this work we present a simple effective model which allows us to assess the long-ranged Coulomb interaction as well as Hubbard interaction. The basic assumption is the existence of a filled valence and an empty conduction band whose properties do not depend on the fill-

ing of the boundary states. The model can be justified by a) extended states are separated from the degenerate boundary states by an energy gap for any confined system, b) minimization of the classical electrostatic energy favors the occupancy of the boundary states, c) at low energies the density of states is strongly dominated by the boundary states. We note that Hartree and exchange interactions between valence band and boundary states are taken into account. Finally, the interaction between electrons occupying boundary states is treated exactly via exact diagonalization of the corresponding Hamiltonian.

Our results are the following: (i) Both interactions give similar results close to half filling, however, there are deviations away from half filling, (ii) Our effective model conserves all symmetries of the full Hamiltonian and can be expressed in terms of low energy states only, (iii) The initially flat band of boundary states acquires a finite dispersion due to interaction effects, (iv) There is a finite regime around half-filling, where the edge is maximally polarized, i.e., the edge is magnetic, (v) Strong spin features are predicted for low electron (hole) concentration, which should strongly affect the transport properties as they may cause spin blockade through graphene islands. In the following we first introduce our model and then the main results are discussed. Finally we present the conclusions of our work.

Edge states. While an ideal graphene sheet has a vanishing density of states at half filling, real samples have localized states at (or around) zero energy, which are induced close to edges, impurities, defects or wiggles. As a concrete example of a finite set of localized states, we choose the boundary states formed at the zigzag edge of a carbon nanotube : [5, 6]

$$\phi_n = \sqrt{1 - 4 \cos^2(k_n/2)} \sum_{j=0}^{\infty} [-2 \cos(k_n/2)]^j a_{jk_n} \quad (1)$$

Here, $k_n = 2\pi n/N$ denotes the wave number parallel to the edge, N is the number of *A*-sites at the edge and a_{jk_n}

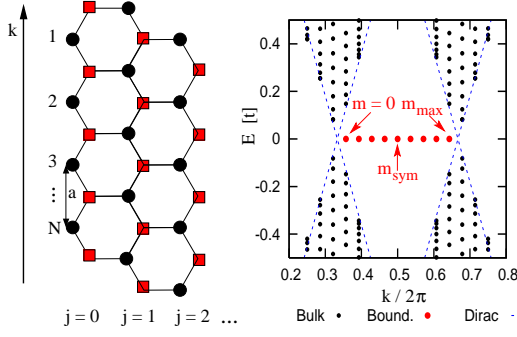


FIG. 1: (Color online) Left: Atomic structure of an unrolled nanotube with zigzag edges. j labels the zigzag lines, each containing N different A and B sites. k denotes the wavenumber along the edge. Right: Single-particle spectrum for $N = 28, N_B = 9$. Red circles denote boundary states, black circles extended (bulk) states and blue dashed line shows the Dirac cone. Boundary states are labeled by integer quantum number m .

is a plane wave with momentum k_n living on the A -atoms of the j -th zigzag line, see Fig. 1. Boundary states exist for all integer numbers n between $n_{\min} = \text{Int}(N/3 + 1)$ and $n_{\max} = \text{Int}((2N - 1)/3)$. From now on the boundary states are labeled by the integer number m , which we call angular momentum, $k_m = (n_{\min} + m)2\pi/N$ with $0 \leq m \leq m_{\max} = n_{\max} - n_{\min}$ as illustrated in Fig. 1. N_B denotes the number of boundary states.

We note that the boundary states of Eq. (1) are the zero energy eigenstates of the original tight binding Hamiltonian describing graphene, without any linearization around the K -points. Thus we also account for interaction induced scattering between the two K -points, which is particularly important for the boundary states. Since the system is invariant under exchange of the two K -points the energy spectrum is symmetric around $m_{\text{sym}} = m_{\max}/2$ as illustrated in Fig. 1. We note that boundary states decay fastest for $m = m_{\max}/2$.

Interactions. We now study the electronic and magnetic properties of the boundary states if either Hubbard V_H or Coulomb interaction V_C is included:

$$V_H = U \sum_i \left(n_{i\uparrow} - \frac{1}{2} \right) \left(n_{i\downarrow} - \frac{1}{2} \right) \quad (2)$$

$$V_C = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} (n_i - 1)(n_j - 1) + V_H \quad (3)$$

here i, j denote the lattice sites, $n_i = n_{i\downarrow} + n_{i\uparrow}$ the occupation of site i with electrons and \uparrow, \downarrow the direction of the spin. The constant charge density of the positive charge background is subtracted from the electronic density, which guarantees charge neutrality at half filling and establishes electron-hole symmetry around half filling. The Coulomb interaction consists of a long-ranged part (first part with $i \neq j$) and the Hubbard part where

the ratio between both is determined by $(e^2/a)/U$ [18].

The single particle spectrum of graphene has a sublattice symmetry. To each states ψ_v with energy $E_v < 0$ there exists a state ψ_c with energy $E_c = -E_v$ and vice versa. The states are related by $\psi_c(\mathbf{r}_i) = \epsilon(\mathbf{r}_i)\psi_v(\mathbf{r}_i)$ with $\epsilon(\mathbf{r}_i) = -1$ if \mathbf{r}_i is a B-site and $\epsilon(\mathbf{r}_i) = 1$ otherwise. We note that $\psi_v(\mathbf{r})^* \psi_v(\mathbf{r}') = \psi_c(\mathbf{r})^* \psi_c(\mathbf{r}')$. Therefore we can write the completeness relation as

$$2 \sum_v \psi_v(\mathbf{r})^* \psi_v(\mathbf{r}') + \sum_m \psi_m(\mathbf{r})^* \psi_m(\mathbf{r}') = \delta_{\mathbf{r}, \mathbf{r}'}, \quad (4)$$

where v denotes the (orbital-)index for the valence band and m for the boundary states.

The interaction between the filled valence band and the boundary states can be written as $H_{VB} = \sum_m E_m n_m$, where Eq. (4) allows to express the potentials E_m in terms of boundary states only,

$$E_m = - \sum_n \langle nm | V | nm \rangle + \frac{1}{2} \sum_n \langle nm | V | mn \rangle. \quad (5)$$

V is either Hubbard $V_H(\mathbf{r}_1, \mathbf{r}_2) = U \delta_{\mathbf{r}_1, \mathbf{r}_2}$ or Coulomb interaction $V_C(\mathbf{r}_1, \mathbf{r}_2) = e^2/|\mathbf{r}_1 - \mathbf{r}_2|$. Since there is no kinetic energy, the effective Hamiltonian for the boundary states consists only of the potential term H_{VB} and the mutual interaction between electrons occupying boundary states. We note that the sublattice symmetry allowed us to account for the interaction with the valence band without calculating the finite energy eigenstates. In fact, even for a finite energy window around the Dirac points one can express all interactions in terms of the low energy states within that energy window. The interaction between electrons occupying boundary states is treated exactly by numerically diagonalizing the Hamiltonian matrix. Since our effective model conserves the symmetries of the full Hamiltonian, we can diagonalize the Hamiltonian matrix in subspaces of given spin, angular momentum and particle number denoted as S, S_z, M, N_e . Since the energy is independent of the spin projection we set $S_z = S$. Furthermore we note that electron-hole symmetry around half filling is also conserved.

Within our model, the empty band of boundary states has zero energy. Since H_{VE} is diagonal in the basis of boundary states the eigenenergy of a single electron occupying a boundary state is given by E_m of Eq. (5), which consists of a Hartree term (first part) and an exchange term (second part). One can also define a band structure at half filling, where the ground state is maximally spin polarized. The energy \tilde{E}_m needed to add (or annihilate) an electron (or hole) to the ground state at half filling by occupying the boundary state $|m\rangle$ is given by

$$\tilde{E}_m = \frac{1}{2} \sum_n \langle nm | V | mn \rangle. \quad (6)$$

It only consists of the exchange part. The energy bands are depicted in Fig. 2.

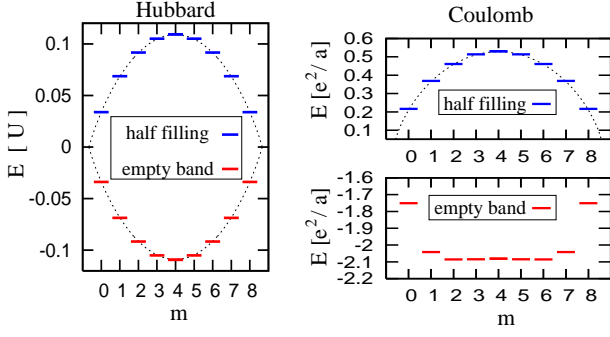


FIG. 2: (Color online) Band dispersion E_m for empty band (see Eq. (5)) and half filled band \tilde{E}_m (see Eq. (6)) for $N = 28, N_B = 9$. Dashed lines show continuous limit ($N \rightarrow \infty$).

For Hubbard interaction exchange and direct term are the same so that $E_m = -\tilde{E}_m$ with:

$$E_m = -\frac{U}{2N} \sum_n \frac{(1 - 4 \cos^2(k_m/2)) (1 - 4 \cos^2(k_n/2))}{(1 - 16 \cos^2(k_m/2) \cos^2(k_n/2))}$$

Here $k_m = (n_{\min} + m)2\pi/N$ as explained below Eq. (1). These energies rapidly converge for large N to a band of boundary states as shown in Fig. 2. The maximum of the band is at $m = m_{\text{sym}}$ ($k = \pi$) and the bandwidth is given by $U(\sqrt{3}/2\pi - 1/6) \approx 0.11U$. Close to a K -point the dispersion of the boundary states is given by $\pm \hbar v_F k U / 3t$, where k denotes the distance from the K -point.

For Coulomb interaction, exchange and Hartree term are different. The exchange interaction is short-ranged and converges fast in the limit of a long edge as illustrated in Fig. 2 for the band at half filling. However, the Hartree term has a long-ranged contribution that leads to a $\log(N)$ divergence of the Hartree contribution to the potentials E_m . Already the band structure shown in Fig. 2 indicates that close to half filling the results obtained by either Hubbard or Coulomb interaction will resemble each other, while differ results can be expected close to an empty or filled band of boundary states.

Results. As discussed earlier, the effective model for the boundary states conserves all symmetries of the full Hamiltonian. We note that it is crucial to include the Hartree and exchange one-body potentials induced by the interaction with the valence band.

Fig. 3 shows the spin of the ground state (red line) and energy gap for spin excitations (black line) as a function of the number of electrons occupying boundary states. We find that close to half-filling the system is maximally polarized, whereas far away from half filling, i.e. close to the empty or filled band, the addition of a single electron or hole leads to strong alternations of the spin of the ground state. The energy gap for spin excitations shows an odd-even effect in the particle number and is generally bigger close to half filling.

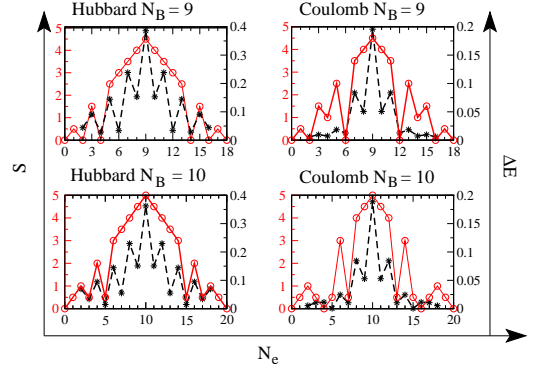


FIG. 3: (Color online) Spin of the ground state (red) and energy gap for spin excitations from the ground state (black) as a function of the number of boundary electrons. Upper and lower row correspond to $N = 28, N_B = 9$ and $N = 31, N_B = 10$ respectively. Energies in units of e^2/R (Coulomb) and U/N (Hubbard).

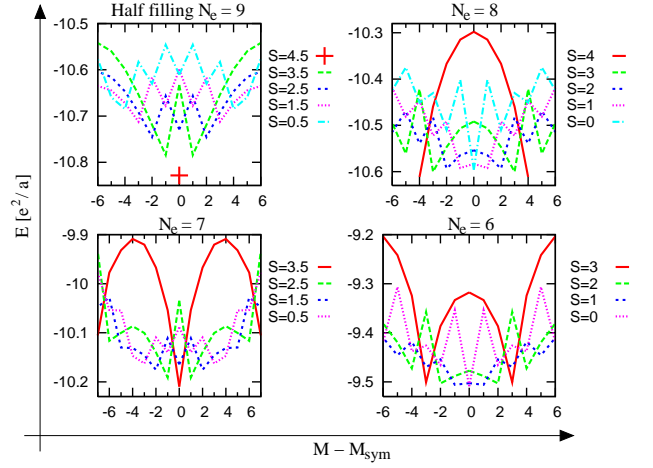


FIG. 4: (Color online) N_e -electron ground state energies as function of total spin S and angular momentum M ($M_{\text{sym}} = N_e m_{\text{sym}}$). The favored spin depends on the angular momentum. For certain occupation numbers (e.g. $N_e = 8$) the ground state has a finite angular momentum. $N = 28, N_B = 9$.

The underlying physics is determined by the competition between the minimization of the interaction energy on the one hand and of the single-particle energies on the other hand. This competition is most obvious for the Hubbard interaction, where only electrons of opposite spin interact with each other so that the interaction between boundary states always favors a spin polarized ground state. On the other hand the interaction with the filled valence band leads to a dispersion of the band of boundary states as illustrated in Fig. 2 and a spin unpolarized state allows for a double occupation of energetically preferred orbitals.

While close to half filling the spin polarized state is al-

ways favored, we find for a nearly empty band of boundary states that the reduction in potential energy can exceed the cost in interaction energy, so that the spin unpolarized state is favored. Furthermore, we note that there is an odd-even effect in the particle number shown in Fig. 3, which is caused by the symmetry of the band structure around $m_{\text{sym}} = m_{\text{max}}/2$ illustrated in Fig. 2, which leads to a kind of shell structure in the single-particle energies.

Coulomb and Hubbard interaction strongly resemble each other at half filling where the system is charge neutral and the physics is governed by the short-ranged exchange interaction. Away from half filling, however, the structure of the charged edges is dominantly determined by charge correlations which are different for Coulomb or Hubbard interaction.

Conclusions and outlook. We have presented a scheme to study the electronic structure of midgap states at arbitrary filling, including the effects of interactions. Examples are boundary states or states localized near vacancies, cracks, or wiggles, etc. close to half-filling. In our model all interactions are expressed in terms of midgap states, and it is exact under the assumption of an inert, filled valence band.

We have applied our model to the localized states at zig-zag edges, where the effects of interactions have been extensively studied, mostly using short-ranged couplings like an onsite Hubbard term and mean field techniques. We have not considered in detail effects due to the existence of two edges in a graphene ribbon. However, we note that the boundary states of different edges are not coupled by Hubbard interaction. Treating the kinetic coupling perturbatively one then finds that an antiferromagnetic alignment of the two edges is favored, in agreement with previous work [10, 19, 20]. We expect the same behavior for Coulomb interaction at half filling.

We found that the ground state close to half filling is spin-polarized for both Hubbard and Coulomb interaction, which is in agreement with earlier calculations. However, for a low electron (hole) occupation we predict strong alternations of the total spin with the number of boundary electrons and furthermore we find different behavior for Hubbard or Coulomb interaction. The limits can be approximately described as a one dimensional ferromagnet, near half filling, and a Wigner crystal when the midgap states are almost empty.

In both limits, near half filling and an almost empty midgap band, interactions lead to an effective one particle band which is dispersive, with a bandwidth which has a well-defined limit when the length of the edge is much larger than the lattice spacing. Hence, the boundary states acquire a finite velocity, and can contribute to the transport properties of the system. We have considered clean systems with no disorder. At half filling the low energy states have a well-defined valley polarization and currents are valley polarized at each edge. All possi-

ble backscattering processes therefore require intervalley scattering, which is usually significantly smaller than intravalley scattering [21].

For certain fillings (see $N_e = 8$ in Fig. 4), the ground state is a doublet with two possible values of the linear momentum. If the edge is shaped into a ring, this result implies that, for these fillings, the ground state has a persistent current of a mesoscopic size, as the current, $j \propto \partial E / \partial \phi$ where ϕ is an applied flux in a cylindrical geometry, scales approximately as R^{-1} , where R is the length of the edge. As discussed above, the decay of this current in samples with disorder is controlled by intervalley scattering.

Our results also show that the spin of the lowest energy state depends strongly on the total linear momentum of that state. This situation resembles the dependence of the spin on total angular momentum in atoms and quantum dots with circular or spherical symmetry.

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